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The Search for Alternative Refrigerants -- A Molecular Approach

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THE SEARCH FOR ALTERNATIVE REFRIGERANTS--A MOLECULAR APPROACH

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ABSTRACT

The impending production limitations on the fully halogenated CFC refrigerants is causing an intense search for possible substitutes. This study reviews the historical development of the CFC refrigerants and the relationship between molecular structure and the ozone depletion and greenhouse warming potentials. It then demonstrates that the halogenated hydrocarbons (a class of compounds that includes the CFCs) remain the most promising candidates for replacements based on both theoretical thermodynamic arguments and an empirical data base search. The inevitable practical tradeoffs among the various candidates are seen to vary in a systematic fashion based on molecular structure.

LA QUÊTE POUR UNE ALTERNATIVE AUX ACTUELS REFRIGERANTS - UNE APPROCHE MOLÉCULAIRE

RESUMÉ

Les limitations prévues dans un proche future sur la production des refrigerants du type CFC totalement halogénés out causé une intense quête pour des possibles substituents. La présent etude résume le dévelopment des refrigerants CFC jusqu'à ce jour et leur relation entre leur structure moleculaire et l'epuisement de l'ozone ainsi que leur effets de sérre potentials. Ie est ensuite démontré que les hydrocarbones halogénés (une classe de composés que inclue les CFC) restent les candidats les plus prometteurs pour les replacements; ceci est base sur des arguments théoriques de thermodynamic ainsi que des recherches empiriques sur des bases de données. Les compromis inévitable entre les aspects pratiques des différents candidats semblent varies d'une façon systematic basée sur leur structures moleculaires.

THE SEARCH FOR ALTERNATIVE REFRIGERANTS - A MOLECULAR APPROACH [1]

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The advent of the international agreement limiting production of certain refrigerants because of their detrimental effects on the atmosphere has caused a sudden and intense concern in the refrigeration and air conditioning industry. With a decision now made as to which refrigerants will be affected and how much production will be cut, it appears that substitutes for trichlorofluoromethane (R11) and dichlorodifluoromethane (R12) will have to be developed. Although there is little doubt that such a development will be possible there is no doubt that the substitutes will compromise some of the qualities or properties possessed by the current refrigerants. The type and extent of these tradeoffs can have great influence on the form of solution the industry and public take. Therefore, it is essential that there be full knowledge of the properties of these new refrigerants and the impact their different properties will have on systems in the field.

Just as tradeoffs are inevitable so are limitations. With all the advances that have been made in this and other industries over the years, it is easy to delude oneself into thinking that anything is possible if only enough research and development effort is applied. This is <u>not</u> true. There are very definite limitations on the number and type of fluids that can reasonably act as refrigerants. This has been known since the development of the first chlorofluorocarbon (CFC)[2] refrigerant some 60 years ago and all of the research on the subject since then has not altered that opinion except for very special applications of limited use.

Recently, much attention has been paid to several new compounds that may serve as alternatives. But information concerning these new refrigerants is somewhat fragmentary. In particular, the underlying, fundamental reasons why a specific compound is presented as a replacement for R11 or R12 are missing. One is left wondering what other possibilities remain undiscussed. This leads to uncertainty on the part of equipment manufacturers contemplating the substantial capital investment involved in redesigning products to use a different refrigerant. While they may be willing to make such an investment once, they would want some assurance that the chosen alternative will not itself be replaced in a few years.

The objectives of this paper are to present the criteria required of a refrigerant, discuss the reasons why CFCs were originally investigated as refrigerants (reasons which also make them the most promising in the search for alternatives) and finally to demonstrate that the inevitable tradeoffs among the various alternatives can be treated in a systematic way.

THE CFC/ATMOSPHERIC PROBLEM

Much has been written on the subjects of ozone depletion and greenhouse warming and only a very brief overview is given here. The interested reader is referred to the extensive compendium of research compiled by NASA [1] or the excellent summary presented in reference [2].

The so called 'ozone layer' actually consists of ozone present at very low concentrations in the stratosphere between 7 and 28 miles in altitude. Ozone, or O_3, is formed by the interaction of ultraviolet radiation from the sun with molecular oxygen (O_2). Harmful UV-radiation is absorbed during this formation process and also directly by the O_3 once it is formed. Ozone is unstable and will eventually revert back to O_2. The presence of chlorine in the upper atmosphere will, through a

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[1]This is a modified version of a paper previously published as "Quest for Alternatives," ASHRAE Journal 29 no. 12, Dec., 1987. Reprinted with permission.

[2]In this article 'CFC' will refer to a carbon-based compound to which chlorine, fluorine and/or hydrogen are attached. By this definition, some CFCs contain no chlorine and others no fluorine. All numerical designations will be prefixed by 'R' (for refrigerant) in accordance with ANSI/ASHRAE Standard 34-78, avoiding the varied and often confusing nomenclature (e.g., CFC-11, FC-134a) which is now appearing.

complicated series of chemical reactions, catalyze the destruction of ozone and thus upset the balance between its continuous creation and destruction.

The chlorine-containing CFC refrigerants are one source of chlorine but only if they survive in the troposphere (lower atmosphere) intact for the many years necessary for a gas emitted at the earth's surface to be transported to the stratosphere. Compounds which are broken down quickly in the lower troposphere are washed out by rain. Thus, the ozone depletion potential of a refrigerant is related not only to its chlorine content but also to its atmospheric lifetime which has been shown to be a function of its hydrogen content.

The problem of global warming due to the greenhouse effect has received far less attention recently than that of ozone depletion but is felt by many to be equally important [1,2]. The greenhouse effect refers to the trapping by the atmosphere of infrared radiation emitted at the surface and the subsequent warming of the earth's climate. While the greenhouse effect is often associated with carbon dioxide from the combustion of fossil fuels, it is now estimated that other trace gases including nitrous oxide, methane and CFCs have a combined greenhouse effect equal to or slightly greater than CO_2. Although the atmospheric concentrations of CFCs are several orders of magnitude smaller than carbon dioxide they absorb strongly in the infrared, particularly in the wavelengths between 7 and 13 μm where the atmosphere is otherwise largely transparent. This absorption is due to the carbon-chlorine and carbon-fluorine bonds present in CFCs and will take place as long as the molecule is intact.

Just as the problems of ozone depletion and greenhouse warming associated with CFCs can be traced to their molecular structure so too can the solution. Throughout this paper a fundamental approach based on molecular structure will be taken in the search for alternative refrigerants.

REQUIREMENTS OF A REFRIGERANT

The working fluid in a vapor compression refrigeration system must satisfy a number of requirements as discussed by Threlkeld [3] and ASHRAE [4] and summarized in Table 1. The most essential characteristic is chemical stability within the refrigeration system--all the other properties would be meaningless if the material decomposed or reacted to form something else. Stability can be a double-edged sword; once emitted to the atmosphere a refrigerant should not be so stable that it persists indefinitely. The ideal refrigerant would be totally stable in use but decompose within a few years in the atmosphere due to conditions (such as ultraviolet radiation or reactive chemical species) not present in the sealed system.

The next most important characteristics relate to health and safety. As specified in the ASHRAE Safety Code for Mechanical Refrigeration [5], in residential and most commercial applications a refrigerant must be nonflammable and of a very low order of toxicity. These can be compromised in some industrial applications as evidenced by the use of hydrocarbons and ammonia. The toxicity and flammability classification of refrigerants is dealt with in ASHRAE Standard 34 [6,7]. The new

TABLE 1 - Refrigerant Criteria

Chemical:	Stable and inert
Health, Safety and Environmental:	Nontoxic Nonflammable Does not degrade the atmosphere
Thermal:	Critical point and boiling point temperatures appropriate for the application Low vapor heat capacity Low viscosity High thermal conductivity
Miscellaneous:	Satisfactory oil solubility High dielectric strength of vapor Low freezing point Reasonable containment materials Easy leak detection Low cost

environmental requirement must be added to the traditional health and safety criteria. A refrigerant should not contribute to ozone depletion, low level smog formation nor greenhouse warming.

The thermodynamic and transport properties determine the performance of a refrigeration system. We will demonstrate below that the critical or boiling point temperatures and the heat capacity of the vapor are the most significant thermodynamic criteria. These two fundamental criteria account for all the desirable properties usually presented, such as high latent heat of vaporization, positive evaporator pressure, etc. By considering only the most fundamental thermodynamic criteria it is possible to establish a link between bulk properties and molecular structure; this will yield insight into the type of molecule most likely to be a good refrigerant.

A number of other more practical criteria are also necessary or, at least, desirable. High oil solubility and high vapor dielectric strength are most important for hermetic compressors. A freezing point below the lowest expected system temperature is necessary. Finally, compatibility with common materials of construction, easy leak detection, and low cost are obviously desirable.

Finding a new refrigerant is thus seen to be no small task. For a refrigerant to be used as a direct substitute in existing equipment virtually all of the above criteria must be satisfied. At most, some compromise in thermal properties could be tolerated at the expense of performance. For an alternate refrigerant for a newly designed system the situation is not as critical since equipment could be adapted for the different pressures and capacity that would accompany a change to a refrigerant with a different boiling point; heat exchangers could be adjusted for different transport properties; and the system could be constructed of different materials. Even in this case, however, it seems unlikely that compromises could be tolerated in the areas of chemical stability, and health and safety.

HISTORICAL DEVELOPMENT OF THE CFC REFRIGERANTS

In the early years of refrigeration the available refrigerants were less than satisfactory; all were either flammable or toxic or both. In 1928, Thomas Midgley, a research engineer with a subsidiary of General Motors, was asked to see if he could develop a nontoxic, nonflammable refrigerant that would function well as a working fluid for the home refrigerator. As it was put to him, " . . . the refrigeration industry needs a new refrigerant if it is ever to get anywhere" [9]. His initial reaction was that no single compound could satisfy these requirements but that a mixture of a nontoxic but flammable material with one that was nonflammable but toxic might yield a nonflammable mixture of moderate toxicity.

Midgley, along with his associate Albert Henne, turned to the periodic table of the elements to find a solution. When arranged according to the number of vacancies in the outer shell of electrons, patterns became apparent. A majority of the elements were metals in their elemental form and formed nonvolatile ionically-bonded compounds when combined with other elements. Only the non-metallic elements formed compounds that were sufficiently volatile to be considered. But among these, many could be eliminated because they formed toxic and unstable compounds. Others, the noble gases, such as helium and neon, are so stable that form very few compounds and by themselves have normal boiling points that are much too low.

This left Midgley and Henne with just eight elements: carbon, nitrogen, oxygen, sulfur, hydrogen, and the halogens fluorine, chlorine, and bromine. They further noticed general trends of flammability and toxicity decreasing as one moved from left to right and from bottom to top in the periodic table. These trends, along with an erroneous entry for the normal boiling point of carbontetrafluoride (R14) in the International Critical Tables, led them to consider fluorine compounds. The high stability of the carbon-fluorine bond further restricted their search to carbon-based compounds. They suspected that the listed boiling point for carbontetrafluoride was in error and also dismissed it as too difficult to make. Instead they decided to try dichlorofluoromethane (R21). Going against the common wisdom of the day they had a hunch that such a compound might be nontoxic. Indeed, within three days of receiving their assignment Midgley and Henne had synthesized a small quantity of R21 (based on a method developed in the 1890's by Swarts in Germany) and demonstrated that it was of low acute toxicity. (Later tests would reveal that R21 is toxic upon long-term exposure.) What followed was a very methodical evaluation of a large number of chlorofluorocarbons culminated by a dramatic introduction of R12 at a meeting of the

American Chemical Society in 1930: Midgley inhaled a lung-full of the new refrigerant and then used it to extinguish a candle [9].

This was the beginning of the modern refrigerants as we know them today. All of them are composed of the same eight elements identified by Midgley. If we apply the new environmental criteria we can shorten the list to seven because bromine is considerably more reactive with ozone than even chlorine.

DATA BASE SEARCH

Taking a completely different approach from that of Midgley, in an unrelated project for NASA, we, at NBS, have searched a proprietary data base of 860 industrially important fluids. In this project the goal was to identify the best fluid for use in a two-phase heat transport system to be installed in space stations. The initial screening criteria are, however, equally applicable for a refrigerant in a vapor-compression system:

1) freezing temperature < -40°C (-40°F)
2) critical temperature > 80°C (176°F)
3) vapor pressure @ 80°C < 5.0 MPa (735 psia)
4) latent heat x vapor density > 1.0 kJ/ℓ (27.8 Btu/ft^3)

The first two criteria insure that the fluid can exist in the two phase region in the temperature range of interest. The third criterion eliminates fluids that would require excessively heavy construction. The final criterion is an approximate measure of the capacity in a refrigeration system. The numerical value was chosen to be within an order of magnitude of currently used refrigerants; for comparison the values for R22 and ammonia are 8.0 and 8.9 kJ/ℓ (222 and 247 Btu/ft^3) respectively.

Of the 860 fluids contained in the data base, 51 passed the screening. They include 15 hydrocarbons (e.g., propane and butane), 5 oxygen compounds (e.g., dimethylether and formaldehyde), 5 nitrogen compounds (e.g., ammonia and methylamine), 3 sulfur compounds (e.g., sulfur dioxide), 4 miscellaneous compounds and, finally, 19 halocarbons (a group of compounds which includes the CFCs as well as bromine containing compounds) including R22, R12, R11, R114, R13B1, R142b and R152a. Of these, all of the fluids outside of the halocarbons are either flammable or toxic or both. While some of the halocarbons are also toxic and/or flammable only this group contains compounds that are both nonflammable and of low toxicity.

There are, of course, other nontoxic, nonflammable materials which can be used as refrigerants, but these are generally useful only at much lower or higher temperatures than the typical refrigeration or air conditioning application. Examples would be helium, nitrogen, carbon dioxide and sulfur hexafluoride for low temperatures and steam at high temperatures. Some of these fluids might also be used at intermediate temperatures but in cycles other than the traditional vapor compression cycle.

It is also interesting to note that, with two exceptions, all of the 51 fluids which passed the screening contain no elements other than carbon, nitrogen, oxygen, sulfur, hydrogen and the halogens fluorine, chlorine and bromine. These are exactly the elements selected by Midgley. The exceptions were the highly reactive and toxic boron trichloride and hydrogen iodide.

Because our database was not exhaustive, compounds of hydrogen and the halogens with elements other than carbon were considered [10]. From within Midgley's list of candidate elements the compounds of sulfur and nitrogen which satisfy thermodynamic criteria tend to be toxic and chemically reactive. Midgley did not include compounds of silicon in his list (much of what is known about silicon chemistry post-dates his work). None of the dozen silicon compounds included in our database passed the screening but, because of some similarities between silicon and carbon chemistry, the silicon compounds were explicitly considered. The most volatile silicone (hexamethyldisiloxane) has a normal boiling point of 99.6°C (211°F); this is much too high for most applications. All the silicon analogs of the CFCs react (sometimes violently) in the presence of water. Indeed all silicon compounds with sufficiently low normal boiling points (e.g. Si_2H_6; T_{boil} = -14.5°C (6°F)) are water sensitive. A major group of silicon compounds that are chemically stable and nontoxic are the tetraalkylsilanes. The most volatile of these, tetramethylsilane, $(CH_3)_4Si$, has a boiling point of (26.5°C) 80°F; this is very similar to that of R11 but this compound is flammable and fails other thermodynamic criteria.

THERMODYNAMIC CRITERIA

Let us now consider in detail the fundamental thermodynamic requirements of a refrigerant. While Midgley's analysis greatly restricted the elements from which one might construct a refrigerant molecule, a huge number of compounds can be synthesized from these few elements. Even restricting the search to the chlorofluorocarbons, one could start with any of the hundreds of known hydrocarbons and substitute fluorine and/or chlorine for one or more of the hydrogens. However, thermodynamic criteria will immediately limit the multitude of possibilities that must be considered.

A recent study at NBS [11] has shown that the refrigerant critical temperature and vapor heat capacity are the key thermodynamic criteria in determining the performance of the theoretical vapor compression cycle. For a fixed set of condenser and evaporator temperatures, as the critical temperature is increased the volumetric heating or refrigerating capacity refrigerant (defined as the capacity per unit volume of refrigerant vapor entering the compressor) decreases. This is due to the lower vapor pressure and thus lower vapor densities (at a given evaporator temperature) for refrigerants with higher critical temperatures. The coefficient of performance (COP), however, is increased for refrigerants with higher critical temperatures. Or equivalently, the COP drops as the temperature of the condenser approaches the critical temperature of the refrigerant. This points out the fundamental tradeoff between high capacity and high efficiency one must face in choosing a refrigerant.

A property related to critical temperature is the normal boiling point, the temperature at which the vapor pressure equals one atmosphere. This will be used in most of this article rather than the critical temperature because of the greater familiarity and availability of data for the normal boiling point. It is also an excellent thermodynamic index. Since most fluids (and certainly CFCs) have nearly parallel vapor pressure curves when plotted as a function of temperature, the normal boiling point is a good indicator of vapor pressure at all temperatures and thus the operating pressures in a system. The normal boiling point is also a good indicator of the critical temperature since the ratio of T_{boil} to T_{crit} is 0.6-0.7 for most fluids. The conclusion is that in order to have a similar capacity, efficiency and operating pressures, a replacement refrigerant will have to have a similar boiling point temperature.

The heat capacity of the vapor, C_p^o, has a lesser effect on performance than the critical temperature but is still significant. (The heat capacity used in this analysis is evaluated in the limit of zero pressure at the critical temperature.) The heat capacity affects the performance of the vapor compression cycle primarily through its influence on the shape of the two-phase region or 'vapor dome' on a temperature-entropy diagram as shown in Figure 1. (This figure also shows a typical vapor compression cycle.) Low values of C_p^o give a vapor dome such that a compression process starting on the saturated vapor line terminates in the superheated vapor region; excessive superheat reduces efficiency. With a high value of C_p^o, however, the vapor dome is 'undercut' so that a compression process terminates in the two-phase region. Such a 'wet' compression must be avoided for most types of compressors. The liquid and vapor sides of the two-phase region are interconnected and thus high

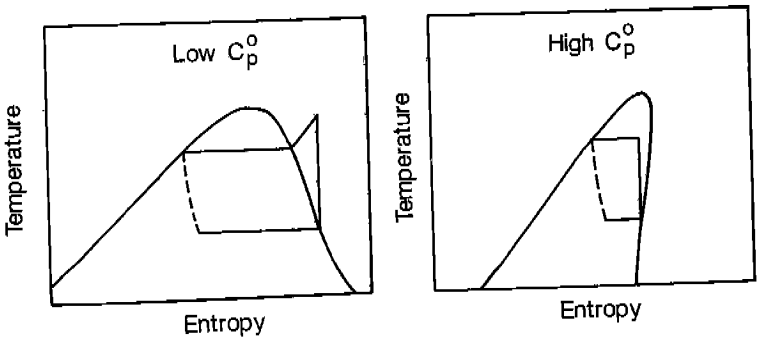

Figure 1 Effect of vapor heat capacity on the shape of the two-phase region on temperature-entropy coordinates.

values of C_p^o also result in greater flash losses in the expansion device. The result of these offsetting effects is an optimum value for C_p^o lying between 40 and 100 J/mol K (9.6 and 24 Btu/lb mol R) depending on the critical temperature of the refrigerant. The optimum value of C_p^o results in a vapor dome that gives a small superheat; this is the behavior obtained with most common refrigerants.

To a first approximation, each chemical bond within a molecule makes a discrete contribution to C_p^o ranging from roughly 11 J/mol K (2.6 Btu/lb mol R) for a carbon-hydrogen bond to 21 J/mol K (5.0 Btu /lb mol R) for a carbon-fluorine bond to 25 J/mol K (6.0 Btu/lb mol R) for a carbon-chlorine bond [12]. Thus the optimum value of C_p^o would be obtained with small molecules such, as CFCs having one or two carbon atoms as a skeleton. But to be useful as a refrigerant, a fluid must have a critical temperature appropriate for the application as well. For a condenser temperature of 35°C (95°F) (typical of many air conditioning, heat pumping and refrigerating applications) a refrigerant critical temperature in the range 65-235°C (149-455°F) is desired. Most of the one- and two-carbon CFCs indeed have critical temperatures in this range.

By contrast, most of the CFCs with three or more carbons have high values of C_p^o and thus vapor domes which imply a 'wet' compression process. Also, they are, in general, much more difficult to manufacture than the smaller molecules and tend to have critical temperatures which are too high for most applications. The few CFCs in this category which have values of C_p^o low enough to avoid a 'wet' compression are flammable. Thus we can restrict our search to the one-and two-carbon CFCs.

EVALUATION OF ALTERNATIVE CFCs

There is little evidence to indicate that the alternative refrigerants will come from other the than CFC family. The theoretical approach of Midgley as well as our own empirical and thermodynamic analyses point to the chlorofluorocarbons as the most promising compounds for use as refrigerants. This class of compounds should not be discarded because of environmental problems with the fully halogenated CFCs. The task facing the HVAC and refrigeration industry is to identify an environmentally benign CFC or CFC mixture which retains as many of the attributes of R11 and R12 as possible.

There are 15 possible one-carbon and (including the different isomeric forms) 55 possible two-carbon CFCs[3]. A means of systematizing the key properties is needed, otherwise one is faced with a seemingly random collection of data and would be frustrated by missing information. We have chosen to arrange the compounds in a triangular pattern according to their molecular structure. The base hydrocarbon (e.g., methane, CH_4 or R50 shown in Figure 2a) is at the top and for each lower row one hydrogen is replaced by a chlorine or fluorine atom down to the fully chlorinated compound (e.g., carbon tetrachloride, CCl_4 or R10) at the lower left corner and the fully fluorinated molecule (e.g., CF_4 or R14) at the lower right corner. The bottom row contains the fully halogenated CFCs--all of the hydrogens have been replaced by the halogens chlorine and/or fluorine.

The first property to consider is boiling point. Among the methane (one-carbon) series of CFCs (Figure 2a) there is a regular pattern of increase in boiling point towards the lower left corner of the diagram. The same pattern is seen for the ethane (two-carbon) series (Figure 2b) although it is confused somewhat by the different isomeric forms. (Isomers contain the same number and kind of atoms but in a different arrangement and are designated by a suffix of a, b, or c. In Figure 2b the range of boiling temperatures is given for the different isomeric forms.) Figure 2 indicates the wide range of boiling points available among the CFC family. For example, there are 6 compounds with a boiling point within (10°C) 18°F of R12: namely, R40, R161, R152a, R134, R134a and R115. But boiling point is not the only criterion that must be satisfied.

The next property to consider is flammability. Here we will consider the flammability in air at normal atmospheric pressure; at other pressures or in the

[3]The CFC compounds containing a carbon-carbon double bond are not considered because of their lower stability. The bromine containing compounds are not considered because of the much greater ozone depletion potential of bromine relative to chlorine.

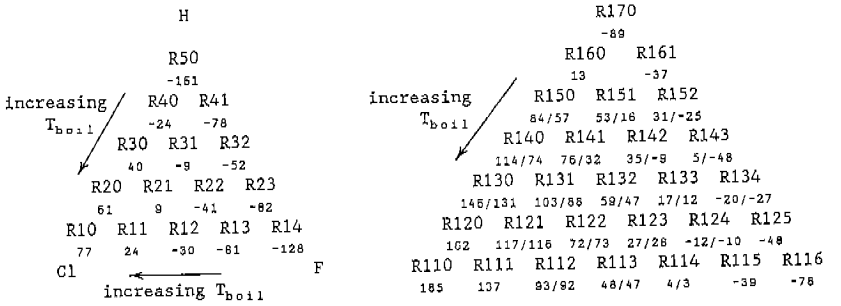

Figure 2 Normal boiling points (°C) for the CFCs arranged according to molecular structure a) methane series (one-carbon) b) ethane series (two-carbon).

presence of other gases, the flammability characteristics may differ. For the methane series (Figure 3a) a very clear pattern emerges; the compounds in the top half of the diagram are flammable while those in the bottom half (i.e., those with more than half of the hydrogens replaced by halogens) are nonflammable. The same pattern is seen with the ethane series (Figure 3b). This latter diagram indicates the usefulness of systematizing properties in this way; because of the clear pattern which has emerged it is possible to infer properties for compounds for which no data is available. For example, although we could not locate flammability data for R121 it is almost certainly nonflammable based on its low hydrogen content and the nonflammability of other compounds around it.

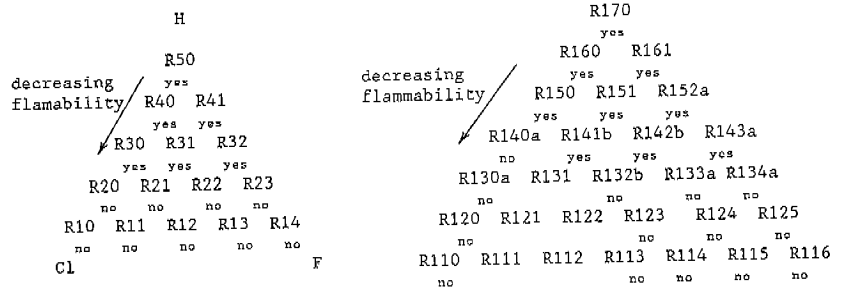

Figure 3 Flammability in air for the CFCs a) methane series b) ethane series.

Toxicity is the property which is least amendable to a simple systematization scheme. Rather than being a simple physical property, toxicity pertains to the interaction of a chemical substance with a living organism. The situation is further confused by the different types of toxic effects such as acute effects from a single but massive exposure versus chronic effects from low-level but repeated exposures. The toxicity of the CFCs is indicated as simply low, moderate or high and while this is a gross oversimplification to a highly complex subject it suits our present purpose. A compound listed as 'low' in toxicity would have only slight effects for both a high acute dose and for long term exposure. A compound of 'high' toxicity would produce serious injury at low levels of exposure. The classification of 'moderate' toxicity would indicate either an intermediate level of acute effect or a toxic effect only upon long-term exposure.

Despite these complicating factors, there is a pattern for the toxicity of the methane-series of CFCs (Figure 4a). The compounds in the lower left (chlorine-containing) region of the diagram are more toxic than those towards the right hand side or upper (fluorine- or hydrogen-containing) regions. The same general trend is seen with the ethane series (Figure 4b) although here there are several compounds such as R133a and R161 that go against the pattern. This emphasizes that, while

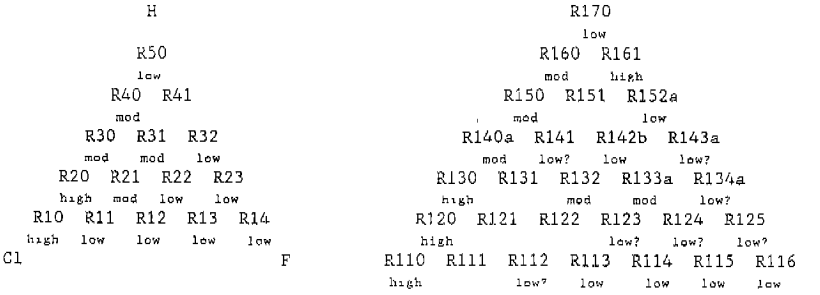

Figure 4 Toxicity for the CFC refrigerants a) methane series b) ethane series ("?" indicates testing incomplete).

generalizations are useful for preliminary screenings, they cannot replace the extensive toxicity studies that must be done to establish the safety of a compound.

The final property to consider is atmospheric lifetime. We have chosen this over an 'ozone depletion potential' or similar index because of the importance of atmospheric lifetime in both ozone depletion and the greenhouse effect. The compounds which are fully halogenated have very long lifetimes. Furthermore it increases with a higher percentage of fluorine, reflecting the great stability of the carbon-fluorine bond. On the other hand, the hydrogen-containing compounds have atmospheric lifetimes which are lower by up to three orders of magnitude, due to the reaction of hydrogen in the molecule with compounds present in the lower atmosphere. Thus the presence of a hydrogen atom in the molecule is seen to be the key for environmental acceptability.

We have demonstrated that the properties of the CFC family of compounds can be dealt with in a systematic fashion based on molecular structure. The tradeoffs are summarized in Figure 5. Although there are a large number of compounds in the CFC family only a limited region in the triangular diagram contains compounds that are simultaneously nonflammable, environmentally acceptable and of low toxicity. It is interesting to note that the new CFCs such as R134a which are receiving much attention lately (as well as R22) do indeed lie within this region. When the additional constraint of acceptable boiling point range is applied, one is left with very few alternatives for any given application. As an example, although 6 CFCs had normal boiling points within 10°C (18°F) of R12 only R134 and R134a are hydrogen-containing and non-flammable; toxicity testing on R134a is incomplete but promising.

Mixtures of refrigerants offer a way to 'tailor' the properties of refrigerant and thus to increase the applicability of what may be a very limited set of acceptable pure refrigerants. Because they offer a way to mitigate an undesirable property of

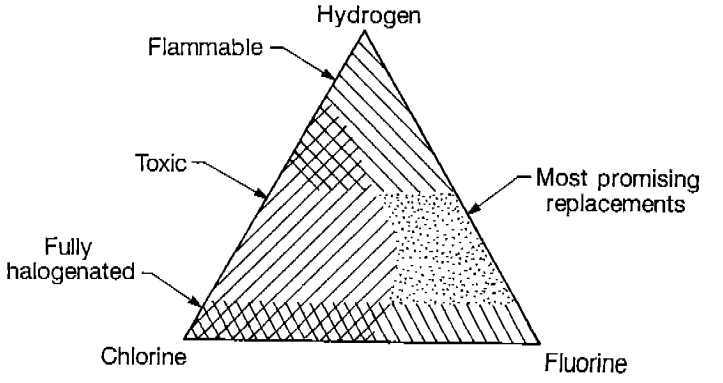

Figure 5 A summary of the tradeoffs among the properties of the CFC refrigerants.

an otherwise acceptable compound, mixtures can expand the list of candidate compounds. For example, R152a is by itself moderately flammable but forms a nonflammable azeotrope (R500) when mixed with R12.

In contrast to the azeotropic mixtures which behave essentially like a pure refrigerant, nonazeotropic mixtures display characteristics (e.g. variable temperature and differing liquid and vapor compositions upon condensation or evaporation) which are unique to mixtures. These characteristics can be exploited to improve performance but generally require hardware modifications. An intermediate class of mixtures--which we have dubbed 'near azeotropes'--do not form azeotropes but behave sufficiently similar to pure refrigerants to allow their use in ordinary refrigeration equipment. Most importantly, the 'near azeotropes' would, by definition, behave such that when a moderate leak would occur, the refrigerant composition would not change enough to cause a significant performance change upon recharging with the original composition.

SUMMARY AND CONCLUSIONS

In the search for alternatives to the fully halogenated CFC refrigerants there are not a limitless number of compounds from which to choose. Rather, it has been demonstrated by both theoretical and empirical reasoning that this same class of compounds--the chlorofluorocarbons--remains the clear choice by virtue of their stability, excellent thermodynamic and health and safety characteristics, and familiarity to both manufacturers and users. However, some of the presently used CFC compounds are no longer acceptable because of environmental considerations. By approaching the problem from the molecular structure, the properties of the various CFC compounds could be treated in a systematic way. This approach revealed a range of CFC compounds (indicated in Figure 5) that should be environmentally acceptable as well as retaining the other attributes of the fully halogenated CFC refrigerants. The initial research efforts should be directed towards CFC compounds from this region or mixtures where the major component is from this region.

The prudent course of action would seem to be to pursue the development of the newer, environmentally acceptable CFC refrigerants (including refrigerant mixtures) along with the necessary equipment modifications as well as efforts to conserve and recycle refrigerants. In as much as some compromise with the traditional criteria (e.g., capacity, efficiency, flammability, etc.) is inevitable some flexibility for compromise with the environmental criteria would also seem to be in order. Radical proposals such as the elimination of R22 (which has only 5% of the ozone depletion potential of R11) should be avoided. Over thirty years of research and development was required to arrive at and maintain the family of refrigerants we have today. A system so much an integral part of our society requires careful scientific and technological planning to effect a significant change. If not, the new 'solution' may bring with it more problems than it solves.

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